General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.

- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.

- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.

- This document is paginated as submitted by the original source.

- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

THE USE AND LIMITATIONS OF THE CONCEPT OF AN EFFECTIVE BINARY DIFFUSION COEFFICIENT FOR MULTI-COMPONENT DIFFUSION

INTRODUCTION

The kinetics of many important processes, e.g., dissolution, precipitation, solid-solid reaction, and homogenization depend on interdiffusion, and frequently technically important systems are multi-component. Fortunately, the phenomenology of multi-component diffusion seems reasonably well understood.[1] However, there have been relatively few examples[2] of unambiguous determination of the matrix of coefficients necessary to describe the diffusion process in multi-component systems (possibly none in oxide systems) and few[3] efforts to predict, by solution of the simultaneous differential equations of multi-component diffusion, the behavior of a non-uniform multi-component system that is tending toward uniformity. Typically, the determinations and predictions have involved the often questionable assumption of composition independent coefficients.

Because of the complexity of the usual approach, we deem it advisable to critically examine a somewhat simpler approach to multi-component diffusion, involving the concept (perhaps first considered by Hougen and Watson)[4] of an effective

binary diffusion coefficient for multi-component diffusion (henceforth EBDC). Since the EBDC are often used without concern as to their validity, our goal will be to determine the relationship of an EBDC to the matrix of phenomenological coefficients and the appropriateness of an EBDC when used in Fick's equations. It is hoped that this will permit a better understanding of limitations of the EBDC's and lead to increasing utility of the EBDC in appropriate circumstances.

MULTI-COMPONENT SYSTEMS

To be consistent with common usage, a system is termed "multi-component" if it has two or more components that may vary independently, and "binary" if only one component can vary independently. Thus, for example, a silver-gold alloy would be considered a binary unless the defect concentration can vary from its equilibrium value. Then and only then can it be considered multi-component (ternary if there is only one species of non-equilibrium defect). Likewise, an oxide is a binary if it is stoichiometric and contains two cations (although there are three species, two cations and oxygen, electrical neutrality and the fact that the sum of cation fractions is unity reduce the number of species that are independently variable). On the other hand, because it is not stoichiometric, iron oxide, $Fe_{(1-\delta)}O$, which has received so much attention at this conference[5] is also a binary oxide

system even though it has a single cation species. A different viewpoint of $Fe_{(1-\delta)}O$ leading to the same conclusion would be to consider Fe^{++} and Fe^{+++} as different species.

With these definitions, a binary system is one which has "composition space" that is unidimensional, i. e., a single number will describe the composition, X. In general, in a system of r components, compositional space has (r-1) dimensions as the composition, $X = (x_1, x_2 \ldots x_{r-1})$, is given by a set of (r-1) values of the fraction† x_i of the individual components.

A continuous "path" on composition space is given by a one-dimensional set of connected compositions. This is illustrated schematically for a ternary system by Fig. 1a. At a p lar composition, the "direction", ${}_rF_i$ of a continuous path on this space is defined by a set of (r-2) derivatives with respect to x_i, i. e.,

$$ {}_rF_i = (f_{1\,i} + f_{2\,i} \cdots f_{(i-1)\,i} + f_{(i+1)\,i} \cdots f_{(r-1)\,i}) $$

where $f_{ki} = \frac{dx_k}{dx_i}$. (We are not concerned with $f_{ki} \to \infty$ because this has explicit meaning in terms of direction.) Various directions, ${}_CF_B = f_{AB}$, on composition space in a ternary system are shown in Fig. 1b.

Since it will be necessary to refer to positions, paths, and directions in both real space and composition space in the following, an effort has been made even at the expense of awkward language to make clear whether composition space or real

† See following page

space is involved.

MULTI-COMPONENT DIFFUSION

In 1945 Onsager[6] suggested extending Fick's law to multi-component systems by allowing the flux density†, j_i, of species i to be a linear combination of the concentration† gradients, $\nabla\rho_k$, (k = 1 → r) of all species. Reducing this idea to a set of equations relating independent flux densities† (by establishing a reference frame) and independent fraction† gradients ∇x_j (by noting that $\sum_{j=1}^{r} \nabla x_j = 0$) give what has come to be known as the phenomenological equations for multi-component diffusion. For an r component system the following (r-1) equations are obtained

$$j_i = -\sum_{j=1}^{r-1} {}_rD_{ij}\, \rho \nabla x_j \qquad (1)^{**}$$

for i from 1 to r-1

The validity of this linear combination is enhanced by the experimental demonstration that at a given composition the coefficients ${}_rD_{ij}$ appear to be independent of time[7] and direction [2d].

Another approach to multi-component diffusion is to use the concept of an EBDC. For species i the EBDC, $\overset{*}{D}_{im}$, defined as follows:

$$j_i \equiv -\overset{*}{D}_{im}\, \rho\, \nabla x_i \qquad (2)^{**}$$

---

† Concentration, density, fraction and flux density can be defined so as to use any quantity; mols, number, mass, volume to describe the amount of the species, but consistency is essential.

** See following page

is the proportionality constant between the flux density of species i and the product of density, ρ, and the gradient, ∇x_i, of fraction of i.

It is clear that the EBDC, $\overset{*}{D}_{im}$, for species i, treats the system as if all of the other constituents can be combined together as a single species, m, standing for MIXTURE. Thus it is like a binary diffusion coefficient between "i" and the remainder of the constituents. While the notion of an EBDC arose in multi-component gas systems, it has been used, explicitly, in condensed systems.[8]

Conservation of species "i" and assumption of constant density, ρ, allows us to write the (r-1) transient diffusion equations from equation 1 as follows

$$\frac{\partial x_i}{\partial t} = \nabla \sum_{j=1}^{r-1} {}_{r}D_{ij} \nabla x_j \qquad (3)$$

$$i = 1 \rightarrow (r-1)$$

Similar treatment yields the following equations:

$$\frac{\partial x_i}{\partial t} = \nabla \overset{*}{D}_{im} \nabla x_i \qquad (4)$$

$$i = 1 \rightarrow (r-1)$$

from equation 2.

We turn to the relation between the matrix of phenomenological coefficients, ${}_{r}D_{ij}$, and the EBDC, $\overset{*}{D}_{im}$. This is

---

** The reference frame for the flux densities, j_i, must be well-defined and in what follows it is assumed that the reference frame is identical for equations 1 and 2.

readily determined because combination of equations 1 and 2 with the assumption that the gradient of all species is in the same direction in real space yields

$$\overset{*}{D}_{im} = \sum_{j=1}^{(r-1)} {}_{r}D_{ij} \, (dx_j/dx_i) \qquad (5)$$

(The assumption is obviously fulfilled if we are concerned only with diffusion that is confined to a single direction in real space. Henceforth, we confine ourselves to this situation and allow, y, to represent distance in this direction in real space.)

Thus, in principle, the EBDC for species, i, $\overset{*}{D}_{im}$, is calculable from (r-1) values of ${}_{r}D_{ij}$ and the set of r-2 independent components of the direction vector ${}_{r}F_{i}$ on composition space.

In addition to being functions of composition X, the EBDC are also functions of direction ${}_{r}F_{i}$ in composition space. This is not surprising because in an r component system there are $(r/2)(r-1)$ † irreducible independent phenomenological coefficients and only (r-1) independent EBDC. Thus the phenomenological coefficients must be more general.

A linear (Fickean) treatment of diffusion implies that the coefficient, $\overset{*}{D}_{im}$, is independent of the gradient, ∇x_i. Thus for the EBDC to be useful coefficients, in the sense

---

† Actually, although the Onsager Reciprocal Relations do not apply directly to the phenomenological coefficients, along with the thermodynamics they reduce the number of independent coefficients from $(r-1)^2$ to $\frac{1}{2}\, r(r-1)$.

that equations 2 and 4 have their usual meaning, the EBDC must be independent of the gradient, i. e., they must be functions† of composition. Since by definition the phenomenological coefficients, ${}_rD_{ij}$, are functions of composition, according to equation 5 the EBDC, $\overset{*}{D}_{im}$, will be functions of composition if the direction, ${}_rF_i$, is a function of composition.

We know that in general the direction, ${}_rF_i$, cannot be a function of composition, X, because typically there are an infinity of possible directions (see Fig. 1b) at a particular composition. However, for a specific experiment described by its initial and boundary conditions, the direction may be a function of composition. If it is and if the end point compositions are constant, there is one and only one diffusion path for each pair of end point compositions, $X_o^{(-)}$ and $X_o^{(+)}$.

We will now consider the use of the EBDC in three different classes of experiments; (i) steady state, (ii) unsteady without a characteristic length, and (iii) unsteady with a finite characteristic length.

STEADY STATE

In one sense this can be a somewhat trivial consideration, because, by definition, at steady state the diffusion path is a

---

† We use function of composition in the sense that for a given value of the composition there is one and only one value of the function.

function only of the pair of end point compositions $X_o^{(-)}$ and $X_o^{(+)}$. Thus, when these are fixed, the directions are a function of composition, i. e., F = F(X) and the concept of an EBDC is valid for steady state diffusion.

It only remains to inquire whether steady state is ever attained in multi-component diffusion. This is a question which needs an experimental answer. Although an unequivocal experiment (one in which it is shown that the diffusion path remains constant) has perhaps not been conducted, indications are that a steady state is attained in multi-component diffusion.

Steady state in liquid systems can occur from a balance between the diffusive and convective flux densities. For a multi-component system with a velocity, V_y, in the diffusion direction, the assumption of a steady state along with the use of equations 3 and 4

$$V_y \left\{\frac{dx_i}{dy}\right\} = \frac{d}{dy} \sum_{j=1}^{r-1} {}_rD_{ij} \left\{\frac{dx_j}{dy}\right\} \qquad (6)$$

$$V_y \left\{\frac{dx_i}{dy}\right\} = \frac{d}{dy} \overset{*}{D}_{im} \frac{dx_i}{dy} \qquad (7)$$

Solution of these equations is important in analyzing the kinetics of dissolution or precipitation with free or forced convection.

To obtain the flux density of species i from equation 1, requires the solution of (r-1) simultaneous equations

like equation 6. It is clear that this would be a difficult task and it is not known if there are cases for which this has been achieved.

On the other hand, use of the EBDC requires only a single equation (7) to be solved. In the fortuitous case where the EBDC varies only slightly with composition, analytical solutions[9] of equation 7 are available for conditions appropriate to several important processes. Some support for the existence of a steady state in multicomponent diffusion is obtained from the fact that for given end member compositions the $\overset{*}{D}_{im}$ has been found to be independent of V_y.[8a]

UNSTEADY WITHOUT A CHARACTERISTIC LENGTH

So-called infinite and semi-infinite diffusion couples permit the use of the "Boltzmann transformation", $\overset{*}{y} = y/t^{1/2}$, where y is distance in the diffusion direction, because none of the "boundaries" are at some characteristic finite length, L. Substituting this into equation 3 yields

$$\sum_{j=1}^{r-1} \frac{d}{d\overset{*}{y}} \; {}^{r}D_{ij} \frac{dx_j}{d\overset{*}{y}} + \frac{1}{2}\overset{*}{y} \frac{dx_i}{d\overset{*}{y}} = 0 \qquad (8)$$

$$i = 1 \rightarrow (r-1)$$

Solution of (r-1) simultaneous total differential equations of equation 8 has been achieved in ternary systems

(r=3) for cases where the $_{r}D_{ij}$'s are constant[3] and suggestions as to how to proceed when the coefficients depend on composition have recently been advanced.[3d]

The existence of a solution (determined or not) to equation 8 implies that for given boundary conditions, the composition, X, is a function of $\overset{*}{y}$, i. e., $X = X(\overset{*}{y})$. Thus, the diffusion path is a function of the Boltzmann variable, $\overset{*}{y}$.

If we restrict attention to a single phase region (thermodynamically speaking), then there is a one-to-one relationship between $\overset{*}{y}$ and X as every value of composition, X, corresponds to one and only one value of $\overset{*}{y}$. This permits the conclusion that the diffusion path is a function of the pair of boundary conditions to equation 8† (i. e., the end member compositions). With this established, it follows that the direction is a function of composition, i. e., F = F(X), and therefore that the EBDC are valid Fickean diffusion coefficients for unsteady unidirectional diffusion when there is no characteristic length. Thus, rewriting equation 3 as follows

$$\frac{d}{d\overset{*}{y}} \overset{*}{D}_{im} \frac{dx_i}{d\overset{*}{y}} + \frac{1}{2}\overset{*}{y}\frac{dx_i}{d\overset{*}{y}} = 0 \qquad (9)$$

is permissible and solutions from heat transfer and

---

† This conclusion has been verified because it has been found both in multi-component metal[7] and oxide glass systems[10] that the diffusion path in "infinite" diffusion couples does not vary with time.

binary diffusion are appropriate. Because of the simplicity of equation 9 relative to equation 8, it is convenient to use equation 9 along with equation 2 when it is necessary to calculate the flux density of a particular species in unidirectional multi-component diffusion in the absence of a characteristic distance, L.

UNSTEADY UNIDIRECTIONAL WITH A CHARACTERISTIC LENGTH

In so-called finite diffusion experiments where a characteristic length, L, prevents all the boundary conditions and initial conditions being expressed in terms of y^*, equation 8 and 9 cannot be used. The existence of a characteristic length, L, also permits the end member compositions $X_o^{(+)}$, $X_o^{(-)}$ to vary and thus the diffusion path will not be constant. Therefore, we cannot be certain that the directions, ${}_rF_i$, will remain functions of composition during the experiment and, in general, caution need be exercised to assure that a change in end member composition will not markedly influence the EBDC. To consider this point, we rewrite equation 5

$$D^*_{im} = {}_rD_{ii} + {}_rf_{1i}\,{}_rD_{i1} + {}_rf_{2i}\,{}_rD_{i2} + \cdots$$

and notice that either if the changes of direction ${}_rF_i$ are only very slight or if the cross terms, ${}_rD_{ij}$, $i \neq j$ are very much less than the diagonal term ${}_rD_{ii}$, then we still may have D^*_{im} sufficiently insensitive to factors other than composition so as to be useful. Particular care has to be exercised in

cases such as illustrated in Fig. 1b where a component of the direction can reach infinity.

Guy, Leroy and Lindemer,[3d] in considering ternary alloys with the usual phenomenological equations (1) and (3), have shown how, when the ratio of the magnitude of the diagonal term to the cross terms is great, homogenization of lamina of discreet thickness, L, proceeds almost identically to that predicted using a single EBDC.

UPHILL DIFFUSION OF ONE SPECIES

The EBDC for a particular pair of end member compositions can be obtained by making an infinite diffusion experiment and using equation 9 to interpret the results, as in terms of $D_{im}(X)$.

At times,† a species in a multi-component system in a stable single phase region will behave as if its EBDC is < 0. This is sometimes termed "uphill diffusion".[3(c)] It may occur, for example, when the flux of a species is caused primarily by the random "hopping" of other species. It results in a diffusion path or composition space which is "S"-shaped, as shown schematically in Fig. 1a, and has regions where some of the components of the direction (f_{AB} on Fig. 1a) go to infinity.

For an infinite diffusion experiment we have shown that composition is a function of $\dot{y}^*$. To be consistent with Fig. 1 a graph of one component, x_B, of the composition would

† A particularly clear example is found in Path 5 of Fig. 8 and Fig. 9 of reference 2d.

appear as is shown schematically in Fig. 2. This profile of the x_B component vs composition requires drastic behavior of the EBDC for species B as can be determined by expanding equation 9 to obtain

$$\overset{*}{D}_{Bm} \frac{d^2 x_B}{d\overset{*}{y}^2} + \frac{d\overset{*}{D}_{Bm}}{d\overset{*}{y}} \frac{dx_B}{d\overset{*}{y}} + \frac{1}{2} \frac{\overset{*}{y} dx_B}{d\overset{*}{y}} = 0 \qquad (10)$$

Since x_B $(\overset{*}{y})$ is known, it is convenient to write equation 6 as a linear first order differential equation in $\overset{*}{D}_{Bm}$

$$\frac{d\overset{*}{D}_{Bm}}{d\overset{*}{y}} + p(\overset{*}{y})\ \overset{*}{D}_{Bm} = q(\overset{*}{y})$$

$$\text{where} \quad p(\overset{*}{y}) = \left[\frac{d^2 x_B}{d\overset{*}{y}^2} \Big/ \frac{dx_B}{d\overset{*}{y}} \right] \text{ and } q\ (\overset{*}{y}) = \frac{-1}{2}\ \overset{*}{y} \qquad (11)$$

While equation 11 is, in principle, solvable by use of an integrating factor, it is difficult for cases where the concentration profile is similar to that shown in Fig. 2, because as indicated by Fig. 3, p (obtained from the concentration profile of Fig. 2) has discontinuities. An estimate (10) of $\overset{*}{D}_{Bm}$ as a function of $\overset{*}{y}$ can be obtained which is qualitatively consistent with Fig. 3 with equation 7 and also with equation 3. This is shown as Fig. 4 and the bad behavior (discontinuities, infinite values and negative values) is obvious.

The erratic behavior of the EBDC, $\overset{*}{D}_{Bm}$, in special cases, limits its usefulness, i. e., for the diffusion path in Fig. 1a it would be difficult to characterize the functional depen-

dence of $\overset{*}{D}_{Bm}$ on composition. However, two factors moderate this limitation. (1) In a ternary system there is usually only at most a single species in a given experiment that has an EBDC that is erratic. The diffusion behavior of the system can be described by choosing the EBDC of the other two species. (2) Even when the EBDC behaves erratically, it still follows equation 10, and such important values as flux densities integrated across a given plane can be calculated.

SUMMARY

The EBDC approach to multi-component diffusion, (equations 2 and 4) is in no way contradictory to the usual phenomenological approach (equations 1 and 3). In fact, when the gradient vector in real space of all species is in the same direction, the EBDC can be derived from the phenomenological coefficients and the direction F in composition space. Conversely, the $(r-1)^2$ phenomenological coefficients can be determined from the directions and the EBDC of $(r-1)$ experiments. The EBDC are useful for describing mass transport in steady state and transient behavior when the boundary and initial conditions can be described in terms of a variable, $\overset{*}{y} \equiv yt^{-1/2}$, that combines distance and time. They may be useful in other cases as a close approximation of reality, but care has to be taken to be sure that the EBDC are insensitive to factors other than composition before

using them in Fick's diffusion equations (2 and 4).

Using the EBDC we obtain the convenience of having to deal with a single coefficient (the EBDC) to relate the flux density of a species to its gradient (equation 1) or to predict the transient behavior in a particular infinite or semi-infinite diffusion couple experiment, (equation 10). It is much easier (1 experiment) to determine the concentration dependence of an EBDC along the diffusion path in composition space than it is to determine (r-1 experiments at each composition) the concentration dependence of the matrix of phenomenological coefficients along this path.

We do not obtain something for nothing. We have gained convenience of the EBDC at the expense of generality. Thus, while the EBDC may be very useful for characterizing the kinetics of a process in a multi-component system where mass transport is rate controlling, on the other hand it would be impractical to characterize the diffusion behavior at a particular composition by the EBDC, because of their direction dependence. In a ternary, for example, at a specific composition, it requires a matrix of four coefficients* to characterize the diffusion behavior using the usual phenomenological approach. Two EBDC's are required for the same

---

* Only three of these are truly independent.

purpose. These, however, are not simple coefficients, but functions of direction in composition space, and hence they are much less efficient in characterizing the general behavior.

Acknowledgement: The help of Milton Lees, Arun K. Varshneya and the support of NASA, Research Grant No. NGR 36-003-100, are gratefully acknowledged.

Fig. 1 Ternary composition space

(a) A curved diffusion path

(b) Various directions, f_{AB}, on composition space

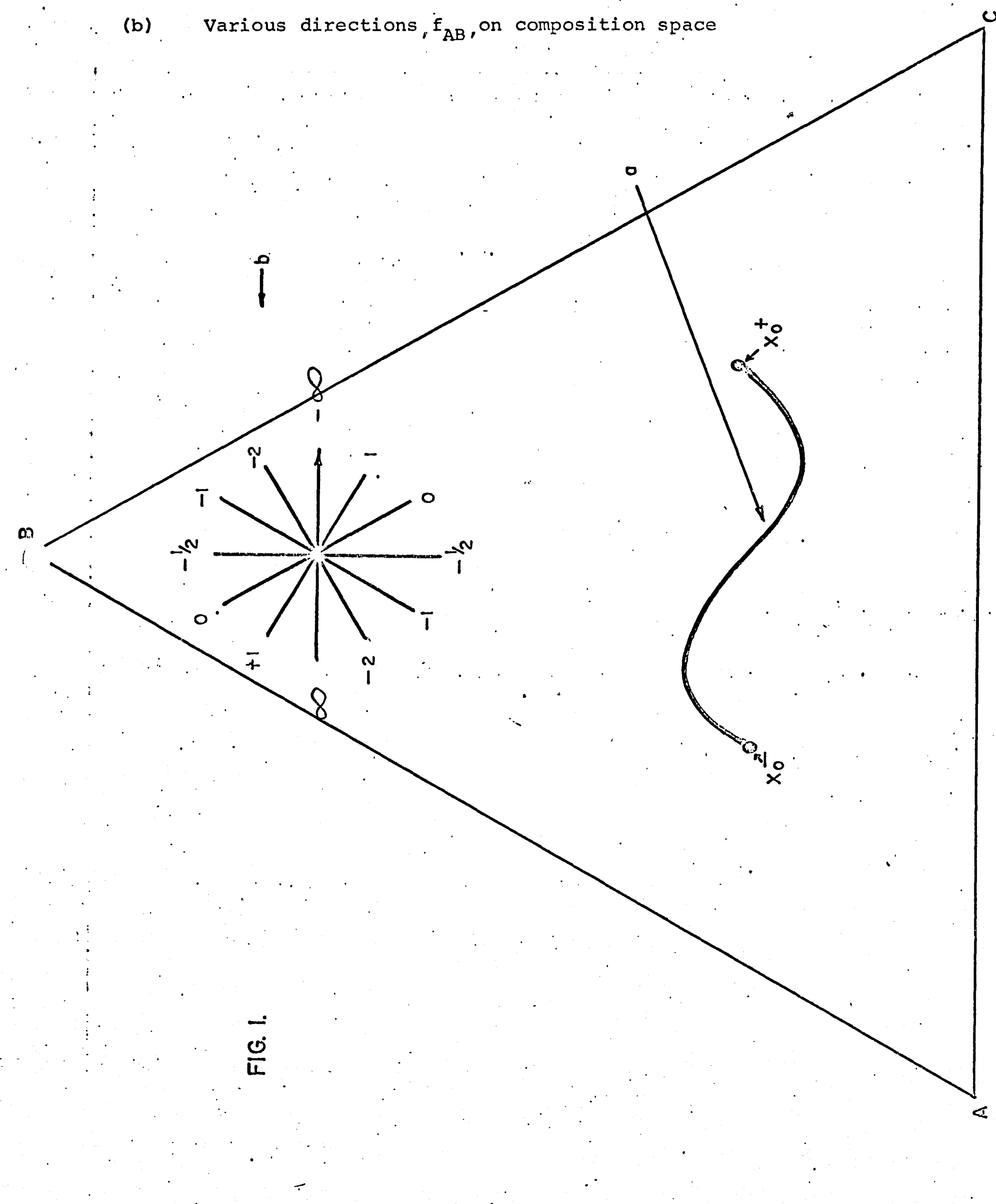


FIG. 1.

Fig. 2 A schematic diffusion profile of fraction of component B, x_b, versus Boltzmann variable, $y^* = yt^{-1/2}$

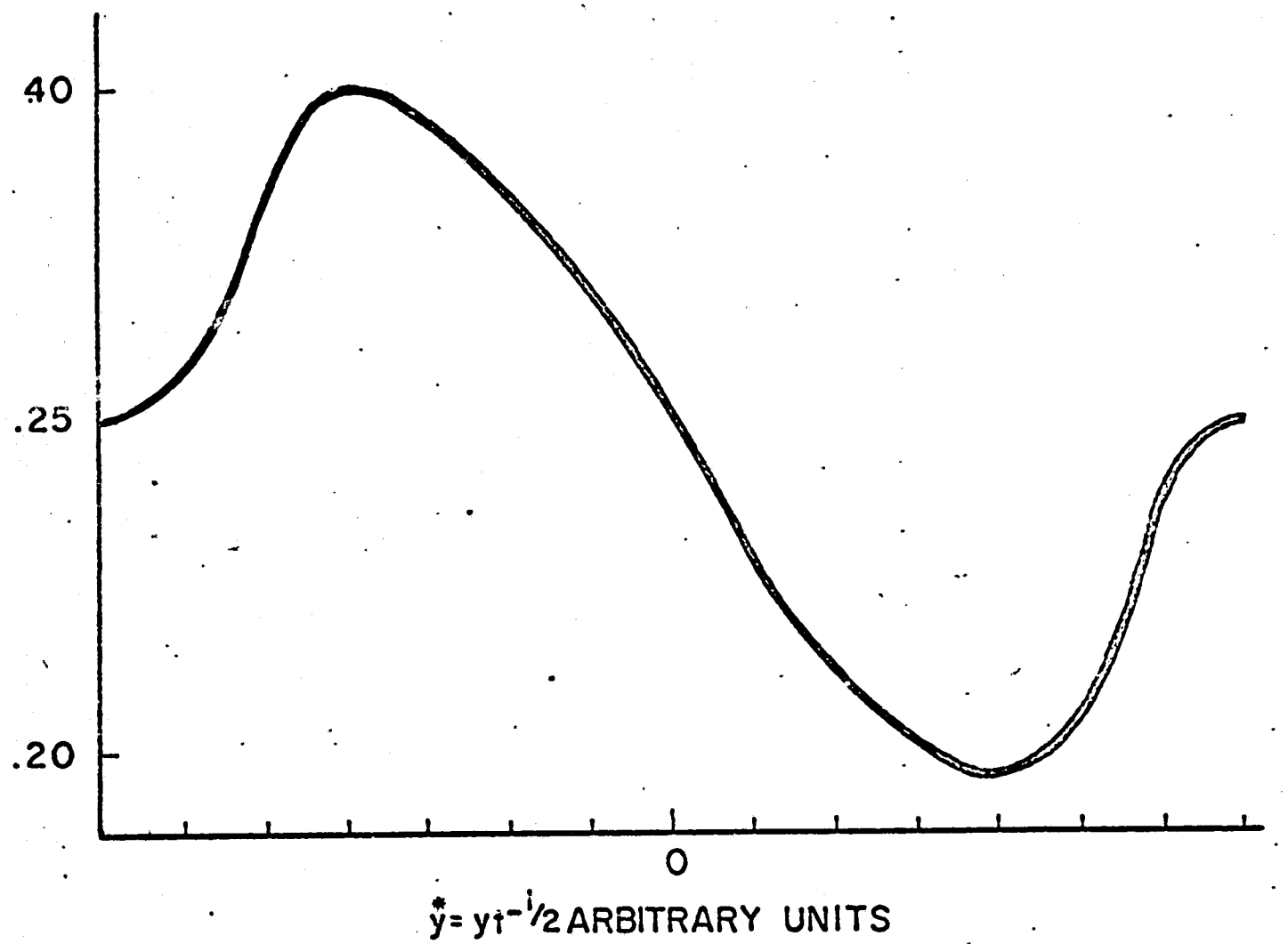
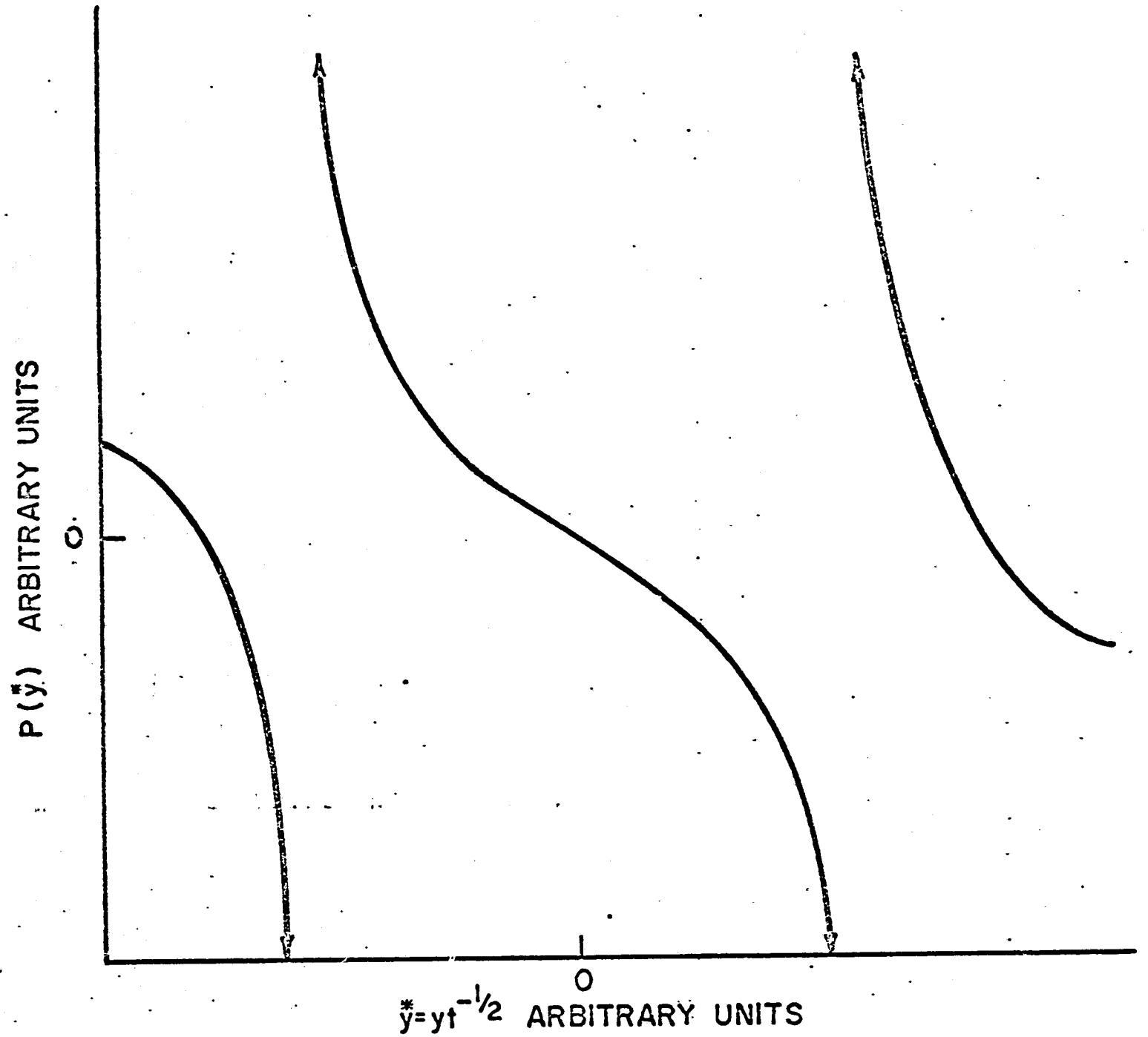


FIG. 2

Fig. 3 Schematic of the function $p(\overset{*}{y})$ versus $\overset{*}{y}$



IG.3

Fig. 4 Schematic of $\overset{*}{D}_{Bm}$ versus $\overset{*}{y}$. (Note $\overset{*}{y}$ scale identical on Fig. 2, 3, 4)

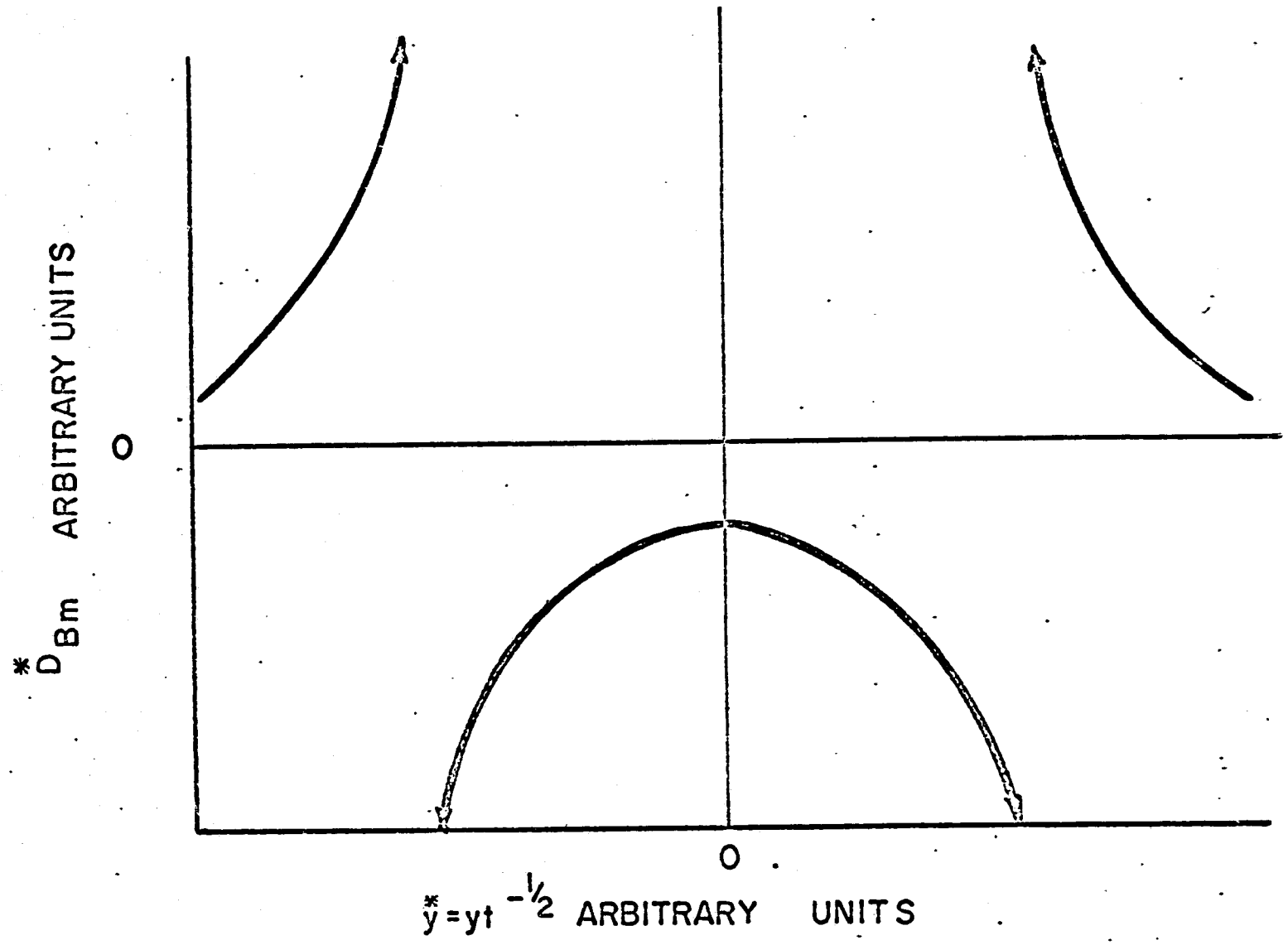


FIG. 4

REFERENCES

1. D. Fitts. Non-Equilibrium Thermodynamics, McGraw Hill Book Company, New York, 1962.

2. (a) J. S. Kirkaldy, G. R. Mason, and W. J. Slater. Canadian Mining & Metallurgical Bulletin, 64, p. 53, 1961.

   (b) A. G. Guy and J. Philibert. Z. Metallkunde, 56, p. 841, 1965.

   (c) T. O. Ziebold and R. E. Ogilvie. Trans AIME, 239, p. 942, 1967.

   (d) J. P. Sabatier, A. Vignes. Memoires Scientifiques Rev. Metallurg., 64, p. 225, 1967.

3. (a) L. J. Fujita and H. Gosting. J. American Chemical Soc., 79, p. 1099, 1956.

   (b) J. S. Kirkaldy. Canad. J. of Physics, 37, p. 30, 1959.

   (c) Y. Oishi. J. Chemical Physics, 43, p. 1611, 1965.

   (d) A. G. Guy, V. Leroy and T. B. Lindemer. A.SM Transactions Quarterly, 59, p. 517, 1966.

4. O. Hougen & K. Watson. Chemical Process Principles, Vol. III, Wiley, New York, 1947, p. 97-99.

5. FeO Paper at Conference. J. B. Wagner, Jr., H. F. Rizzo, et al., L. Himmel and J. B. Holt, R. H. Campbell and M. O'Keefe.

6. L. Onsager. Annals of N. Y. Acad. of Science, 46, p. 241, 1945.

7. T. O. Ziebold. "Ternary Diffusion in Copper Silver Gold Alloys", Doctoral Thesis, M.I.T., Cambridge, Mass., 1965.